

**CRANBERRY INSTITUTE GRANT FINAL REPORT
Phase 2 Studies**

**Use of Lignocellulosic Materials as Sorbents for Pesticide and Phosphate
Residues**

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SUMMARY

In the previous report we presented results of laboratory studies that demonstrated the feasibility of using lignocellulosic sorption media for removing pesticides and dissolved reactive phosphorus from water [1]. In the current report we describe procedures for converting waste bark into useable sorption media in larger batches than before. Larger batches of sorption media are required for field tests scheduled for the summer and fall of 2002.

The conversion procedures consist of physical and chemical processes. Physical processes involve drying the bark chips obtained from a chip mill to 0% moisture content followed by milling to particles of various mesh sizes. Drying can be accomplished by air-drying followed by drying in a drum dryer at elevated temperatures. Milling can be accomplished by using a hammer mill, a rotary knife cutter, or a high speed Pullman dual rotating cutter. Chemical processes involve extracting the bark particles with water containing an environmentally acceptable organic solvent to remove soluble compounds from the bark and to develop its porous structure. After extraction, the bark particles are treated with organic polyelectrolyte solutions. The polyelectrolyte treatment serves to enhance sorption capacity of the bark particles for phosphorus.

Batches of sorption media prepared from bark according to the scheme outlined in the previous paragraph have shown high capacity for removing pesticides and phosphorus from water in the laboratory. The next phase of our work is to test the performance of these sorption media in the field. In this regard, we plan to install filtration units containing these sorption media at a number of cranberry farms in Wisconsin and Massachusetts during the summer and fall of 2002. Each unit will be set up in the “flow through” mode. Typically, wooden planks placed on top of each other control the water head in the bog during winter flooding or wet harvesting. We plan to install the test filtration units immediately downstream of the water head controller. A computer-controlled composite sampler will be placed to sample the water before and after the filtration unit. This will enable us to evaluate how well the sorption media remove pesticides and phosphorus in the presence of natural organic matter in the water released from the bogs.

INTRODUCTION

According to the 1998 National Water Quality Inventory Report to Congress, nutrients and pesticides that originate from agricultural activities are among the leading pollutants affecting rivers and streams in the United States [2]. Thus states and other jurisdictions in cooperation with farming communities, including cranberry growers, are continually seeking better and cost-effective water pollution abatement strategies. The objective of our research is to develop low-cost sorption media for removal of phosphorus and pesticides from water released from cranberry bogs into surface waters. Our approach is to convert low-cost underutilized forest residues such as waste bark or other related chip mill residues into useable sorption media for removal of pesticides and phosphorus in agricultural runoff. We believe that such sorption media will be a valuable addition to the arsenal of best management practices for preventing contamination of surface waters by pesticide or phosphorus runoff from agricultural activities [3].

As we prepared to test these sorption media in the field, it was necessary to develop procedures that would allow us to convert the starting materials in larger batches than the previous small laboratory experimental samples. In the current report we describe physical and chemical processes that we have developed to convert larger batches of waste bark into useable sorption media for the removal of phosphorus and pesticides from water.

EXPERIMENTAL

Materials and Methods

Southern yellow pine bark chips obtained from a chip mill in Kentucky were converted to useable sorption media by physical and chemical processes described below. Physical processes consisted of air-drying followed by oven drying, milling and screening. Chemical processes consisted of extraction with a dilute aqueous solution of N-methylpyrrolidinone (NMP) and treatment with a dilute aqueous solution of polyallylamine hydrochloride (PAA) and epichlorohydrin.

Drying of bark chips

Bark chips were first allowed to air-dry for approximately 4 h by spreading them on a tarp as shown in Figure 1. Thereafter the bark chips were dried for an additional 4 h in a drum dryer at 105°C to drive off the remaining water and some of the volatile extractives. The drum dryer is shown in Figure 2

Milling and screening:

A 200-kilogram batch of oven-dry bark chips was milled and separated into three fractions of different particle sizes on a hammer mill equipped with 30 mesh and 60 mesh steel screens. Processing of the dry bark chips on a hammer mill is shown in Figure 3. The steel screens are shown in Figure 4.

Extraction of bark particles

One kilogram batches of bark particles contained in 70 mm x 330 mm cellulose extraction thimbles were placed in a 10-liter Soxhlet apparatus and extracted with a 10% aqueous solution of NMP to activate the particles and also to remove soluble extractives from the bark. The Soxhlet apparatus is shown in Figure 5.

Chemical treatment experiments

One kilogram batches of air-dry extracted bark particles were placed in a 55 cm x 45 cm x 6 cm Teflon tray and treated with a 1% aqueous solution of PAA and ECH and allowed to react overnight.

Phosphorus sorption experiments:

Sorption experiments were conducted in duplicate by adding 0.1g aliquots of control and modified particles to different 50-mL polypropylene equilibration tubes containing water solutions of sodium dihydrogen phosphate (NaH_2PO_4) in the concentration range, 0.5 mg/L to 100 mg/L. Sodium chloride (NaCl) was used to adjust the ionic strength of the water solutions. The suspensions were allowed to equilibrate for 24 h at 25 \pm 1 $^\circ$ C on a mechanical end-over-end shaker at 7 rpm. After equilibration, the suspensions were allowed to settle for an hour and then filtered through a 0.2- μ m polypropylene filter. The undigested filtrate was analyzed for dissolved reactive phosphorus (DRP) on a Lachat analyzer (Zellweger Analytics, Milwaukee, Wisconsin) by following the standard molybdate-based colorimetric method at a wavelength of 880 nm [4]. An aliquot of the filtrate was digested with concentrated nitric-sulfuric acid to hydrolyze organic phosphorus to orthophosphates in order to determine the total dissolved phosphorus (TDP). Dissolved organic phosphorus (DOP) was calculated from the difference between TDP and DRP.

Pesticide sorption experiments

A 2-gram sample of sorption material, weighed accurately to two decimal places, was placed in a 10.5 X 300 mm glass column and allowed to equilibrate overnight under water. The sorption material in the column was rinsed with five column volumes of water before 500 ml of water, containing 40 ppb each of dichlobenil, chlorothalonil and chlorpyrifos, was percolated through it under gravity flow. The column effluent was concentrated by solid phase extraction on a C-18 cartridge. The concentration of the pesticides in the extract was determined by gas chromatography with mass selective detection (GC-MSD), using a 30-meter DB5-MS capillary column equipped with a 5-meter megabore capillary guard column [5].

Results and Discussion

Drying of bark chips: Air-drying the bark chips for approximately 4 h on a sunny day resulted in bark chips with a moisture content of approximately 20 percent from an initial value of slightly more than 50 percent. Oven drying the air-dried particles at 105 $^\circ$ C resulted in dry particles (0% moisture content) in approximately 4 h.

Milling and screening: Three types of milling and screening technologies were considered. The hammer mill technology was tried first because it is inexpensive, readily available, and has a relatively larger selection of screens that allowed us to produce particles of various sizes. Samples of bark chips milled to different particle sizes are shown in Figure 6. Other technologies that can be used include the rotary knife cutter or the high speed Pullman – dual rotating cutter.

Extraction and activation of bark particles: As shown in Figure 7, the surface morphology of the extracted bark particles is significantly different from that of unextracted particles. The extracted bark surface shows a considerably rougher texture compared to the unextracted bark surface. The effect of surface roughening is activation of the bark particles, which facilitated the interaction of the bark fibers with PAA.

However, it should be noted that the extraction and activation step remains the limiting step in the current processing scheme. The Soxhlet apparatus used for this purpose can only produce 1 kg batches of material. The fabrication of an extractor capable of processing up to 20-kg batches of material per day is almost complete (Figure 8). We plan to begin processing by the end of Spring 2002.

Chemical treatment of particles: Two chemical treatment schemes have been investigated to date. One is based on 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTMAC), and the other is based on PAA. The scheme based on PAA resulted in better removal efficiency for phosphorus compared to the CHPTMAC scheme. Consequently further experiments were conducted on sorption media processed by the PAA scheme.

Phosphorus removal: The percent removal of phosphorus from water is dependent on the phosphate initial concentration, pH and ionic strength of the water solution. As shown in Figure 9, percent removal of phosphate from deionized water was high as 99% at 0.5 mg/L, and decreased to 32% at 100 mg/L. In addition, percent removal of phosphate decreased with increase in the ionic strength of the water solution. The influence of pH on percent removal of phosphate in the pH range 5 – 8 is shown in Figure 10. Percent removal of phosphorus increases to a maximum around pH 6.5 – 7.5, and thereafter decreases slightly with increase in pH. The pH of maximum phosphate removal by PAA-bark overlaps well with typical pH values (6.40 – 6.75) of water released from cranberry bogs.

Pesticide removal: As shown in Figure 11, percent removal of selected pesticides by PAA-bark was generally higher (82 – 96%) compared to raw bark (39 – 88%) or granular activated carbon (51 – 72%). It should be noted however that the relatively lower percent removal of pesticides by granular activated carbon was a result of poor wetting of the surfaces of the granular activated carbon by water. Poor wetting of the surface hinders the transfer of pesticides from water to the sorption medium.

The percent removal of pesticides from water is influenced not only by the surface properties of the sorption medium, but also by the properties of the pesticide such as the octanol/water coefficient, P_{ow} . As shown in Figure 12, the percent removal of pesticides from water by bark increases with $\log P_{ow}$.

Conclusions

Much effort was expended on making the transition from preparation of sorption media in small milligram quantities to kilogram quantities. These transition experiments from small sample sizes to larger batch sizes proved to be more difficult than originally expected. A major contributor to these difficulties is lack of affordable equipment for large-scale extraction of lignocellulosic materials. The Soxhlet apparatus that we are currently using is only suitable for extracting 1 kg batches of material per day. Consequently we have designed, and are in the process of constructing a high-capacity extraction apparatus that will enable us to process as much as 20 kg of material per day.

Future research

As soon as this high-capacity extraction apparatus has been constructed and tested, we plan to install filtration units containing the sorption media at cranberry bogs for field-testing. We expect to leave the filtration units in place at a test site for a defined time period. After obtaining the first set of field test data from these units, we will perform further laboratory-scale tests to determine the influence of other water quality parameters such as turbidity, biological oxygen demand and chemical oxygen demand on the efficacy of the sorption media.

We are also continuing fundamental studies to elucidate the sorption mechanism of modified lignocellulosic materials for phosphorus. These studies will allow us to develop alternative less-costly surface chemistry modification technologies to enhance the sorption capacities of these materials for phosphorus in the presence of natural organic matter in natural water.

We need and are seeking additional funding to:

- ?? Complete the scale-up experiments
- ?? Evaluate hydraulic resistance of sorption media of different configurations such as particle size, pellets or mats
- ?? Evaluate the performance of the sorption media under field conditions
- ?? Evaluate how the properties of these sorption media change over time in service
- ?? Continue fundamental studies on the sorption mechanisms of these materials for phosphorus in the presence of natural organic matter that occurs in natural water.

References

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4. Murphy, J. and J.P. Riley. (1962) A modified single solution method for determination of phosphate in natural waters. *Anal. Chim. Acta.* 27:31-36.
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Figure 1. Air drying bark chips



Figure 2. Drum dryer for drying bark chips at elevated temperatures



Figure 3. Milling oven-dry bark chips in a hammer mill



Figure 4. Hammer mill screens for fractionating bark particles

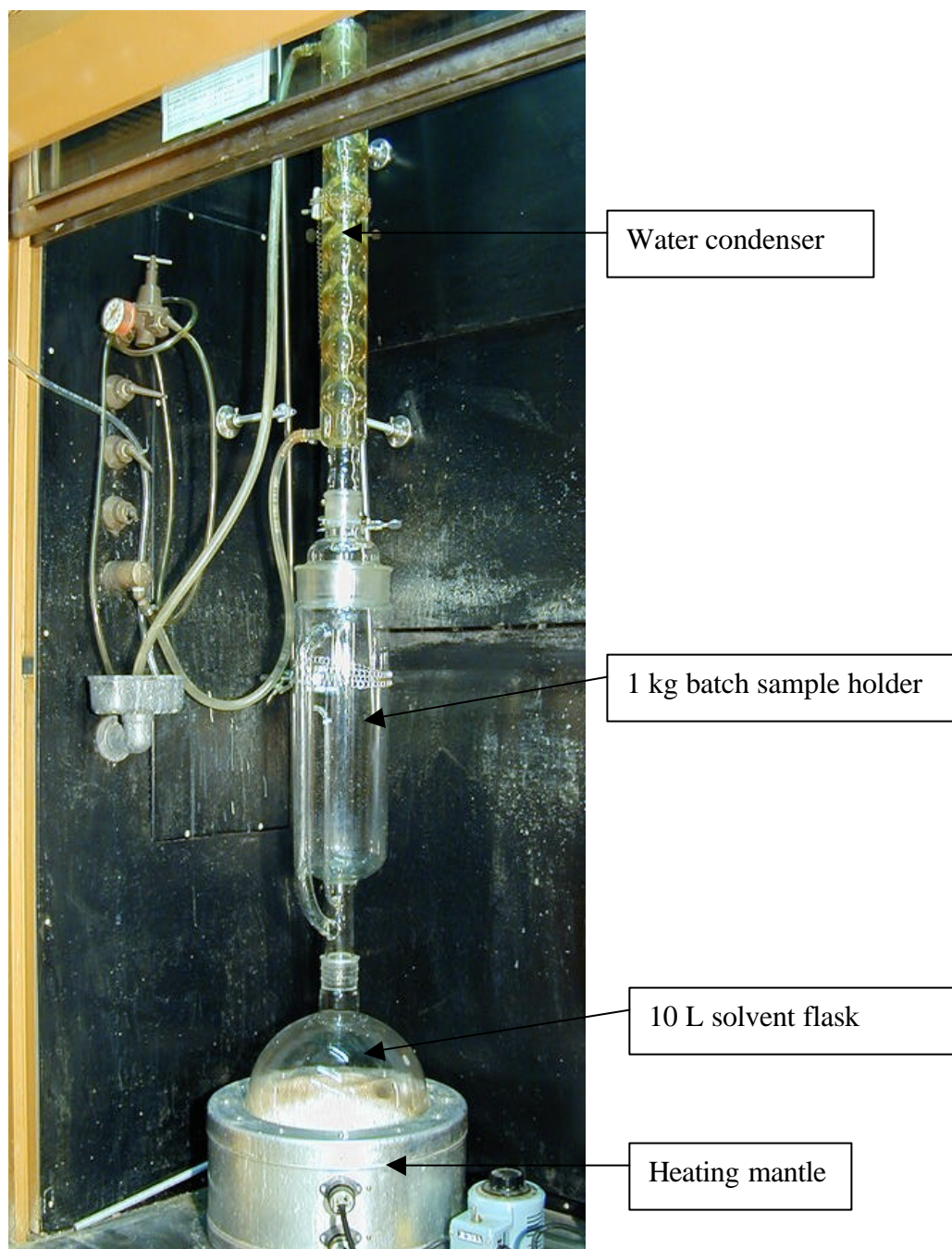


Figure 5. Soxhlet apparatus for extraction and activation of bark particles



Figure 6. Dry bark milled to different particle sizes

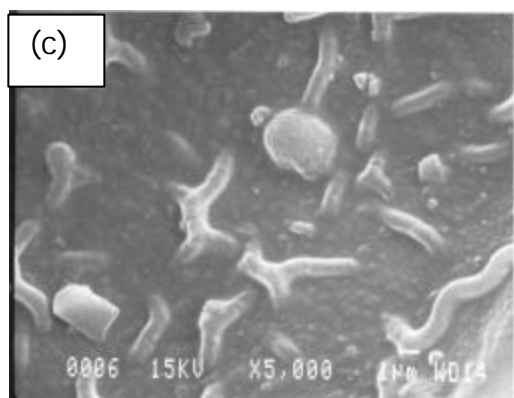
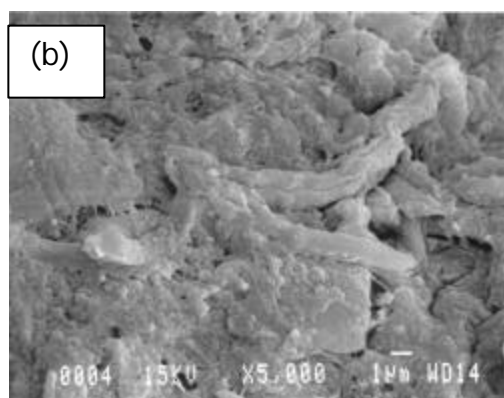
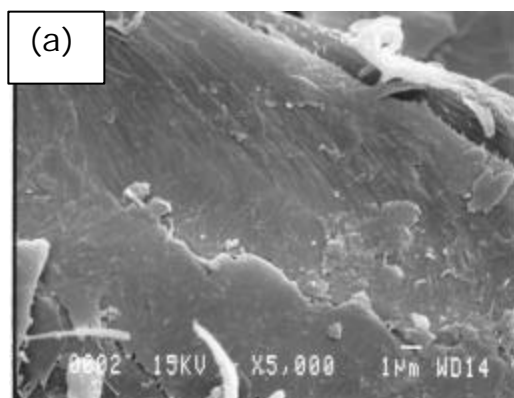


Figure 7. SEM images of bark surface (a) before extraction, (b) after extraction, and (c) after treatment with PAA



Figure 8. High capacity extractor for activation of bark particles

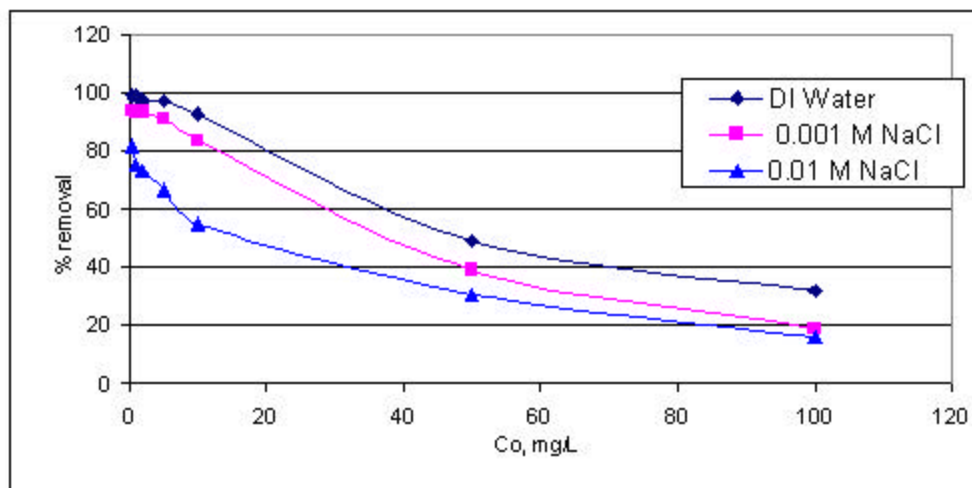


Figure 9. Percent removal of phosphorus by PAA-bark in the concentration range of 0.5 mg/L to 100 mg/L phosphate in water solutions of different ionic strength

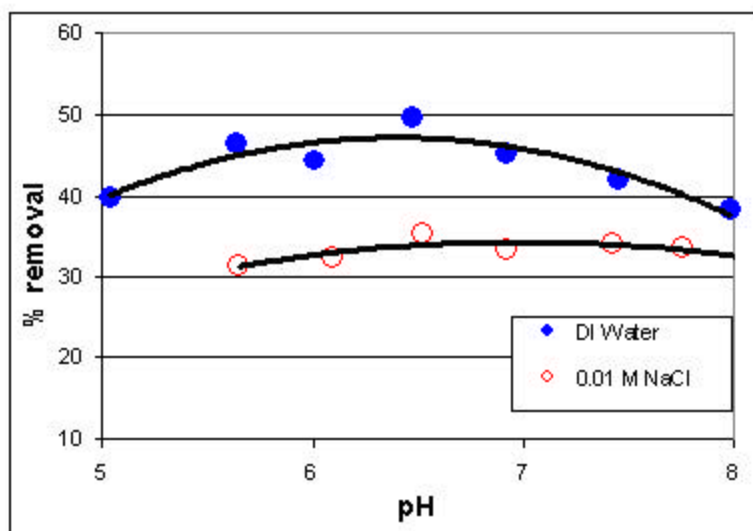


Figure 10. Effect of pH on percent removal of phosphate from deionized water and from 0.01M NaCl solution

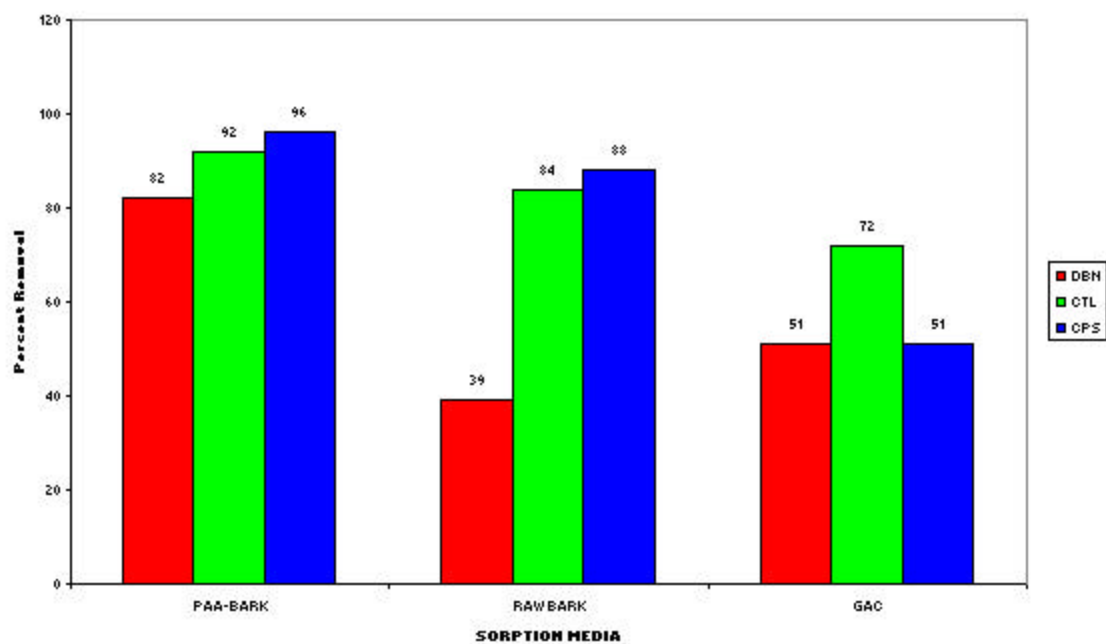


Figure 11. Percent removal of dichlobenil (DBN), chlorothalonil (CTL), chlorpyrifos (CPS) by PAA-bark, raw bark and granular activated carbon (GAC)

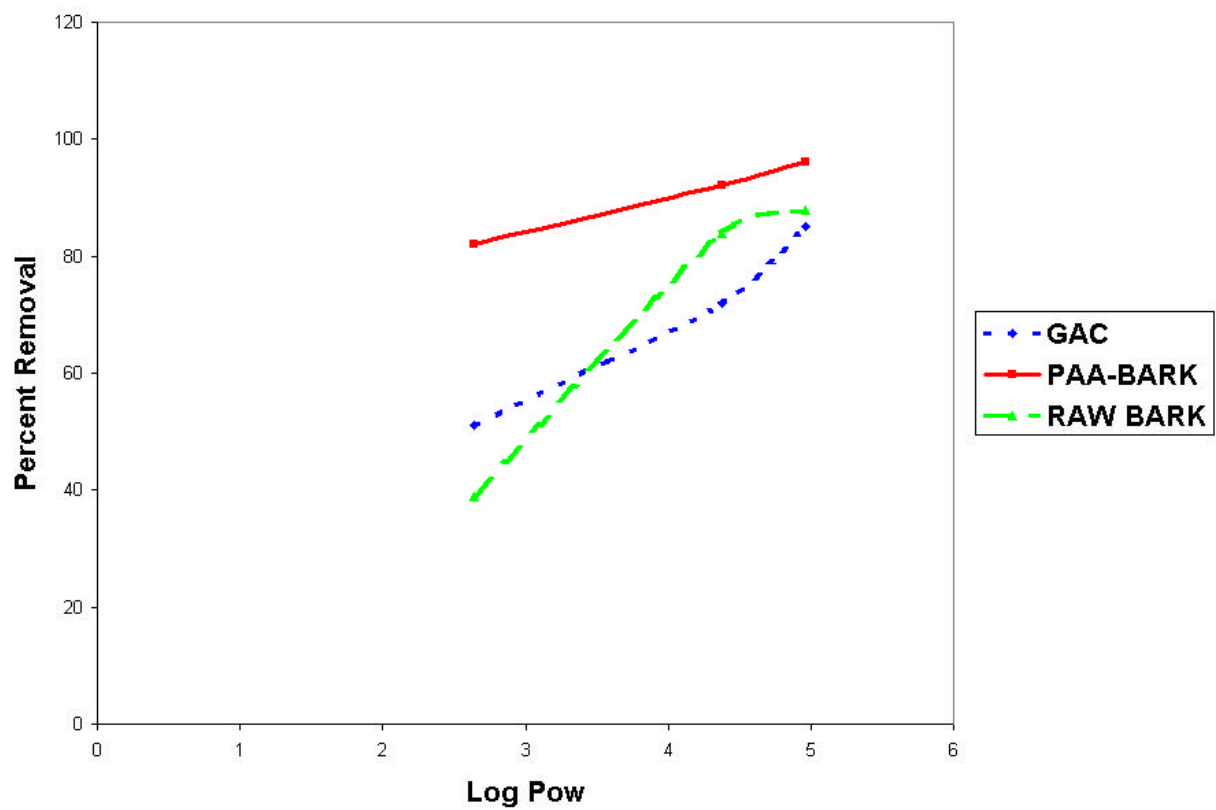


Figure 12. Correlation of percent removal of pesticides to their octanol-water coefficients expressed as Log P_{ow}